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REVIEW ARTICLE

Review of acid rain potential in India: Future threats and remedial measures

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Acid rain is a necessary fall-out of rapid industrialization, urbanization and other developmental activities in India. Acidic deposition is a complex process and can be felt hundreds of kilometers away. Tropical climatic conditions, alkaline-rich soil, desert and sea-derived aerosols, low sulphur content in fuels, etc. coupled with the relatively low industrial growth rate are the foremost favourable factors in preventing acid rain problem in the country as also indicated by several studies in the past. This is in spite of the fact that India is the second largest country, next to China in the Asian continent producing sulphur dioxide emissions. However, the pace of current developmental activities has overtaken these natural favourable factors and as a result, many metropolitan cities are now showing decreasing pH or acidic trends in the precipitation. This paper overviews the present trend, its likely effect, outlines factors contributing to acid rain and suggests possible preventive measures to stop the trend. Projections were made on the basis of RAINS ASIA model to identify areas of potential impact on the ecosystem and identify steps to mitigate the stress factors.

OVER the last few years, there have been important advances in our understanding of the steps which link the emissions of acidic gases such as SO_2, NO_x and HCl to their subsequent deposition and its fall outs. The major contribution to acid rain is reported to be due to sulphur component ($\simeq 70\%$) and oxides of nitrogen ($\simeq 30\%$) though contributions to the acidity of tropical rain from other sources such as organic acids. have also been shown by Keene *et al.*[1]. As there are negligible natural sources of emissions, rapid developmental processes seem to be the main reason for SO_2 and NO_x emissions and subsequently the acid rain potential in India. A high industrial annual growth rate of 4.5% for the current decade (1990–2000) has been estimated in terms of

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Table 1. SO_2 emissions (kt) from area and large point sources and projections, when basic control technologies are used to reduce emission[46]

States/ places	1990 LPS	1990 AREA	2000 LPS	2000 AREA	2010 LPS	2010 AREA	2020 LPS	2020 AREA
Andhra Pradesh	255.37	132.76	375.86	137.89	625.07	280.29	1083.89	467.53
Bengal	165.73	56.53	248.98	111.77	410.36	142.21	698.57	293.94
Bihar	322.64	40.41	436.04	112.17	687.24	264.90	1114.54	436.08
Mumbai	108.82	31.92	203.46	48.69	313.92	66.30	488.64	95.33
Calcutta	27.52	11.84	47.25	30.59	74.87	61.02	130.86	101.42
Delhi	25.32	19.25	48.04	37.10	105.56	67.53	248.16	96.15
EHIM	66.46	0.0	90.52	0.0	141.49	0.0	235.43	0.0
Gujarat	288.79	100.11	404.44	150.64	660.17	294.58	1113.68	547.04
Haryana	84.93	16.54	119.59	35.05	201.26	65.49	362.40	93.60
Karnataka	108.26	25.81	149.35	34.31	249.81	64.74	459.80	93.60
Kerala	55.23	0.0	87.70	0.0	155.54	0.0	278.29	0.0
Chennai	49.52	0.0	90.12	19.09	138.79	59.85	206.28	99.09
Maharashtra	328.16	191.85	480.25	277.36	823.76	418.28	1504.09	614.69
Madhya Pradesh	247.09	164.96	356.91	241.31	588.91	302.16	1024.00	456.45
Orissa	182.78	7.69	250.04	32.44	390.45	91.45	603.73	189.39
Punjab	135.61	43.79	198.33	57.77	344.75	72.98	638.55	112.21
Rajasthan	140.01	21.01	190.64	33.94	305.37	101.79	524.25	201.76
Tamil Nadu	222.42	127.84	332.43	162.20	569.98	260.48	1043.43	435.62
Uttar Pradesh	434.59	206.93	629.86	300.86	1012.73	428.65	1725.51	547.78
WHIM	23.19	0.0	31.45	0.0	51.00	37.42	90.85	92.52
Total	3272.50	1199.24	4771.26	1823.18	7851.03	3080.12	13574.95	4974.20

Table 2. SO_2 emissions for selected countries and its projection (kt)[46]

Country/year	1990	2000	2010	2020
Bangladesh	118.00	164.60	330.29	524.62
Bhutan	1.54	4.50	7.16	11.86
Brunei	6.30	8.41	12.60	18.35
Cambodia	22.19	39.59	75.15	147.47
China	21908.30	34327.85	47840.02	60687.65
Hongkong	139.57	216.26	290.21	377.97
India	3371.74	6594.44	10931.15	18549.15
Indonesia	629.95	1085.07	1868.09	3162.27
Japan	835.49	996.96	1048.26	1119.70
North Korea	343.14	586.11	878.00	1345.43
South Korea	1653.70	2815.37	4046.65	5537.44
Laos	3.35	5,05	7.79	11.68
Malayasia	205.69	242.07	342.35	409.76
Mongolia	77.68	95.05	124.08	167.72
Myanmar	18.09	24.87	32.12	39.60
Nepal	122.33	155.82	193.52	247.44
Pakistan	614.07	1553.47	3683.91	7527.55
Philippines	390.70	626.77	1071.02	2036.90
Seal	243.28	310.44	397.01	511.93
Singapore	190.90	357.67	653.31	1033.20
Sri Lanka	41.88	132.25	170.71	239.02
Taiwan	499.53	765.26	1085.52	1478.68
Thailand	1037.55	1900.94	3276.74	4637.68
Total	33574.97	53008.82	78365.66	109823.07

Gross Domestic Product and this would result into increasingly higher energy demand. Most of our energy demands are met through coal-based sources. In this context, thermal power plants are the major sources of wet and dry deposition of sulphur since sulphur contents in the coal used are found to range between 0.5% and 3%. Petroleum-derived fuels also have sulphur contents. However, the concentration may vary. Crude petroleum usually contains anywhere from 1.0% of sulphur to between 2 and 3% by weight, whereas natural gas, LNG and LPG contain negligible quantities. The total Indian sulphur emissions due to large point and area sources

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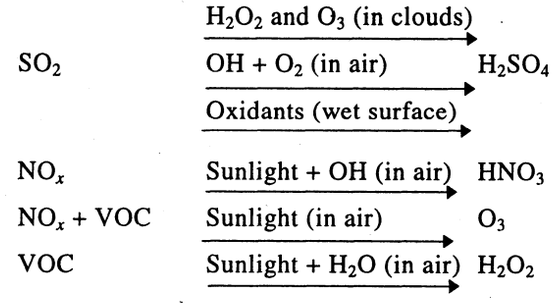
were over 4400 kt in 1990 and are expected to touch the figure of 6500 kt in 2000, 10,900 kt in 2010, and 18,500 kt in 2020 (Table 1) which are second largest in Asia, next only to China with a figure of over, 34,000 kt, 47,000 kt and 60,000 kt in the years 2000, 2010 and 2020 respectively (Table 2). Similarly, increased activities in the transport sector are responsible for NO_x emission. The process is complex and deposition may occur hundreds and thousands of kilometers away from their sources.

In India, tropical climatic conditions and predominantly alkaline-rich soils have a neutralizing effect. The Thar desert in the north-west, the sea and soil-derived aerosols in the coastal areas are responsible for maintaining the pH in the alkaline range in the most parts of India. Higher temperature and sunlight increase the efficiency of atmospheric chemical reactions, particularly those transforming SO_2 and NO_x to acidic sulphates and nitrates. However, the background trends of pH in precipitation have been decreasing all over India[2]. An analysis of data obtained from ten Indian Background Air Pollution Monitoring (BAPMoN) stations collected during the period 1974–1984 shows that a few areas are already under stress conditions[3]. The situation is alarming in and around metropolitan cities of India due to big industrial pockets. In the last two decades, in Delhi alone the precipitation pH has decreased from 7.0 (1965) to 6.1 (1984) and in Agra, from 9.1 (1965) to 6.3 (1984) (ref. 4). Mumbai has shown this trend much earlier. Furthermore, the north-east part of India is likely to become vulnerable to acidic deposition due to the movement of atmospheric pollutants with predominant winter winds from south to north-east India and acidic soil[5]. This region is particularly very rich in forests and bio-diversity. Moreover, the pH values below 5.0 were observed in the silent valley forests[6]. Acid rain may destabilize the entire ecosystem by completely wiping out several forests and aquatic species, thereby distorting the food chain. However, acid rain has much more serious consequences than previously known. In the light of these effects, reviewed here is the situation in India, outlining factors contributing and likely to contribute to acid rain and also suggested possible remedial as well as policy steps to stop the trend.

Acidification

Acidic deposition is defined as the total hydrogen ion loading on a given area over a given period of time generally expressed as keq ha^{-1} yr^{-1} (ref. 7). The total hydrogen ion deposited on a given area over a year may result from acidic rain, acidic snow, acidic gases such as nitiric acid vapour and sulphur dioxide which may dissolve in water films on surfaces producing sulphurous and sulphuric acid. Acidification, therefore, amounts to an increasing supply of hydrogen ions (H^+) and its concentration in a solution is a measure of acidity, which is usually indicated by pH value. A low pH means a high level of hydrogen ions, i.e. the substance is acidic.

Chemical and biological processes, both in soil and water, are badly affected by the hydrogen ion level. There are, however, natural mechanisms opposing a reduction in pH value called buffer action performed mainly by hydrocarbonated watering of various minerals from the rocks etc. As long as calcareous minerals abound in the soil, the pH value will stay fairly high. But if pH value declines, a major buffering process will set in, causing aluminium compounds to dissolve. Free aluminium in the soil not only damages root systems but also leaches out the ground water and surface water, e.g. disappearance of fish in aquatic life due to aluminium poisoning and lowered pH (ref. 8). Concern about acidic deposition has often focused narrowly on sulphur dioxide and nitrogen oxides; however oxidants such as ozone, hydrogen peroxide, and organic free-radicals are intimately associated with and required for production of the mineral acids (sulphuric and nitric). Chief among the pollutants that are emitted as a result of human activities are sulphur dioxides and nitrogen oxides which may land directly on the surface below (dry deposition). In atmosphere, these pollutants can be converted to sulphuric and nitric acids, which come down to earth after being dissolved in cloud and/or rain drops as sulphate or nitrate ions. When this occurs, the fallout is known as wet deposition. The chemical precursors involved in producing acidic deposition are sulphur dioxides and nitrogen oxides and volatile organic compounds (VOCs). The complexities of acidic deposition can be summarized as below[7].



Reaction of the precursors with other chemical entities, often from photolysis, begins immediately on emission, and depending upon the emission rate, weather and concentration in the air of all reactants may proceed at different rates. In the meantime, the pollutants and their products are being transported, diluted, deposited and augmented by new emissions along their path. Deposition at one point from an emission at another location is highly variable. The annual average of all these processes provides a pattern of acidic deposition. Since variation of acidic precipitation over seasons

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and from year to year at a given location is determined primarily by the local and regional climatology, it is difficult to interpret short-term trends or to determine source–receptor relationships empirically.

Emission sources

Sulphur in gaseous form is chiefly formed from the combustion of coal and oil. Everything organic takes up sulphur which explains its presence in fossil fuels. However, oil has 0.1 to 3% of sulphur content by weight[9] while in Indian coal, it is 0.5 to 2%. Natural gas has less than 0.1% of sulphur content. In India, oil consumption increased sharply from 1.1×10^3 mt in 1952 to 54.3×10^3 mt in 1995, appoximately 50 times. Similarly, the capacity of thermal power plants has increased from 2.6 billion k Wh in 1950–51 to 247.7 billion kWh in 1993–94 (ref. 10). This indicates that an estimated 2500 tons of sulphur are being released in the atmosphere due to thermal power plants alone as per data available for 1993–94 thermal power generation. This is 50 times more than that released in 1950–51. Besides house-hold consumption, industrial consumption has also increased. An estimated release of 70% sulphur comes directly from thermal power plants. For the world as a whole, yearly emissions due to human activities are estimated at some 80 million tons in 1995.

Nitrogen oxides on the other hand are formed by the reaction of nitrogen gas in the combustion air with oxygen. Higher the combustion temperature, more is the nitrogen oxides formed. Nitrogen content in fuel also contributes in the formation of oxides. The largest single source is road traffic which has increased tremendously. It is hard to estimate the emission of nitrogen oxide but it has increased many folds in the recent past. NO_x helps directly as well as indirectly in acidic deposition as explained in the previous section. It forms HNO_3 directly with the help of hydroxyl ion and also helps in the formation of ozone which again combines with hydroxyl ion and sulphur dioxide to form sulphuric acid. Use of fertilizers (ammonium) is the second most important source of acidification. Ammonium ions are converted by microorganisms in the soil contributing to acidification. Terrestrial and marine over-fertilization have not only contributed to the process but are also found to cause negative effects in plantations with nitrogen leaking out of the plants due to nitrogen saturation.

Trends of pH of precipitation over India

Geographical and climatic conditions are main advantages with India which provide natural buffering abilities due to the following reasons:

1. Tropical climatic conditions reduce atmospheric CO_2 dissolution in the rain water.
2. The predominantly alkali-rich soil has an additional neutralizing effect.
3. The sea and soil derived aerosols lessen acidic deposition.
4. Higher temperature and sunlight increase the efficiency of atmospheric chemical reactions which decrease the acidic deposition.
5. Aerosols from Thar desert have an alkaline nature which reduces acidic deposition.
6. Indian coal has less sulphur content approximately 0.5 to 2% compared to 3% found in coal of Western countries.
7. India has no significant natural sources of sulphur such as volcanoes, etc.

The acidic sulphates and nitrates are ultimately removed by wet or dry deposition on to the earth's surface. As the rain is in equilibrium with atmospheric CO_2 which yields natural acidity, pH values below 5.6 are considered to be the result of the emission of SO_2 and NO_x (ref. 4). Mukharjee and Krishnanand[11] however, suggested that the natural pH of precipitation would be higher than 5.6 in the tropics due to the lower dissolution rate (about 1.5 times) of CO_2 than that in western countries in the prevailing higher temperatures. To find the trends of pH in India, precipitation data were collected from ten Indian BAPMoN stations listed in Table 3 during the period 1974–1984 as per instructions of the World Meteorological Organization. These stations were located away from industrial sources to minimize the localized or short-term effects.

Evidently, north-west India exhibits higher pH values than the rest of the country (Figure 1). Incursion of sand/dust particles into these areas from the adjacent Thar desert of Rajasthan may be the reason. TSPM measurements at Jodhpur and Srinagar revealed a significant positive correlation indicating that with the increase in the dust content of the atmosphere, pH value of rain water also increases. The regression analysis can be represented by the following equations:

$$\text{pH} = (6.8550 + 0.1216) + (0.0015 + 0.0001)\, c \quad \text{for Jodhpur}$$

$$= (6.7511 + 0.3051) + (0.0042 + 0.0004)\, c \quad \text{for Srinagar,}$$

where c is total suspended particulate matter (TSPM) concentration. These equations indicate that pH value above 6.75/6.85 signifies contribution of TSPM concentration, i.e. soil-derived particulates. During cloud and rain formation, sufficient mixing takes place in the atmosphere and these water-soluble components dissolve in the cloud column, thus making the precipitation alkaline. This explains pH values of 6.7–6.8 for clear and unpolluted environment in India. This is also supported by a comparative analysis made by Khemani *et al.*[3] for coastal, industrial, urban, non-urban areas (Table 4).

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Table 3. Location of BAPMoN stations and pH trends

Station	WMO No.	Lat. Index	Long.	Elev. (m)	No. of observ.	pH Variation	pH Trend	pH Acid rain observ.
Allahabad	42475	25°27'	81°41'	98	56	6.35–9.00	Decreasing	0
Jodhpur	42339	26°18'	81°01'	217	58	6.35–8.70	Decreasing	0
Kodaikanal	43339	10°14'	81°28'	2343	62	5.18–8.70	Decreasing	3
Minicoy	43369	08°18'	81°00'	2	66	5.52–8.90	Decreasing	1
Mohanbari	42314	27°29'	81°01'	111	42	5.50–8.30	No trend	2
Nagpur	42867	21°06'	81°03'	310	42	5.55–8.50	Increasing	1
Port Blair	43333	11°40'	81°43'	79	48	5.65–8.90	Decreasing	5
Pune	43063	18°32'	81°51'	559	76	5.65–8.90	Decreasing	0
Srinagar	42027	34°05'	81°50'	1587	88	6.15–8.40	Decreasing	0
Vishakhapatanam	43150	17°41'	81°58'	72	77	5.92–8.20	Decreasing	0

Table 4. Average concentration in mg l^{-1} of major ionic components and pH values in rain water samples at different stations in India

Station	Cl^{-1}	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	pH	H^+ (μeq l^{-1})
Coastal										
Alibag	5.97	1.11	0.57	0.27	3.84	0.88	2.38	0.60	7.2	0.063
Colaba	4.14	2.58	0.40	0.51	3.12	1.13	2.56	0.64	7.1	0.079
Industrial										
Kalyan	3.95	5.20	1.92	0.38	2.36	1.02	1.86	0.47	5.7	2.00
Chembur	5.0	20.20	–	2.10	2.20	1.10	3.10	0.68	4.8	15.85
Power plant										
Indraprastha	2.06	2.10	3.3	0.93	0.98	0.25	2.03	0.31	5.0	10.0
Urban										
Pune	2.57	1.78	0.48	0.10	1.84	0.20	2.07	0.45	6.3	0.50
Delhi	2.54	2.73	2.54	0.53	1.75	1.28	2.95	0.62	6.1	0.79
Non-urban										
Sirur	2.64	1.53	2.64	0.07	1.84	0.95	3.53	0.80	6.7	0.20
Ranjangaon	2.02	1.53	1.37	0.08	1.81	1.41	3.30	0.96	6.8	0.16

The results obtained and discussed are in good agreement with a host of individual precipitation studies conducted[12–14]. Khemani *et al.*[15] obtained an average pH value in cloud water over Pune region as 6.9 using aircraft observations which they claimed to be similar as obtained in the pollution-free region of USSR and Australia. In these observations, ammonium salts, which are prime acid neutralizers, are not found in sufficient quantity. pH values in industrialized nations in 1978 had been recorded between 4 and 6 (Table 5) which was much lower than that obtained in India. Therefore, the following conclusions based on background trends of pH precipitation may be drawn on the basis of available literature[16].

1. The pH values in precipitation at most of the BAPMoN stations are decreasing. However, it is unlikely to fall in acidic range in future except for those areas where deposition is influenced by industrial belt and power stations.
2. The overall probability of occurrence of acid rain in India is about 2%.
3. The pH value varies between 5.18 and 9.00 and the maximum frequency is 6.5 to 7.0.
4. The soil-derived aerosols from Thar Desert lead to high pH values in north-west India.
5. In a clean dust-free environment, the pH values of precipitation are observed in the range 6.7–6.8 without much variation.

Since BAPMoN stations were located in less polluted areas, it would be worth mentioning the paper of Khemani *et al.*[4] for Agra (27°10'N, 78°02'E, 169 m a.s.l) and Delhi (28°35'N, 77°12'E, 218 m a.s.l), where industries have grown faster (about three times) in the 1980s than in 1960s. Khemani *et al.*[3] also reported a pH of 4.8

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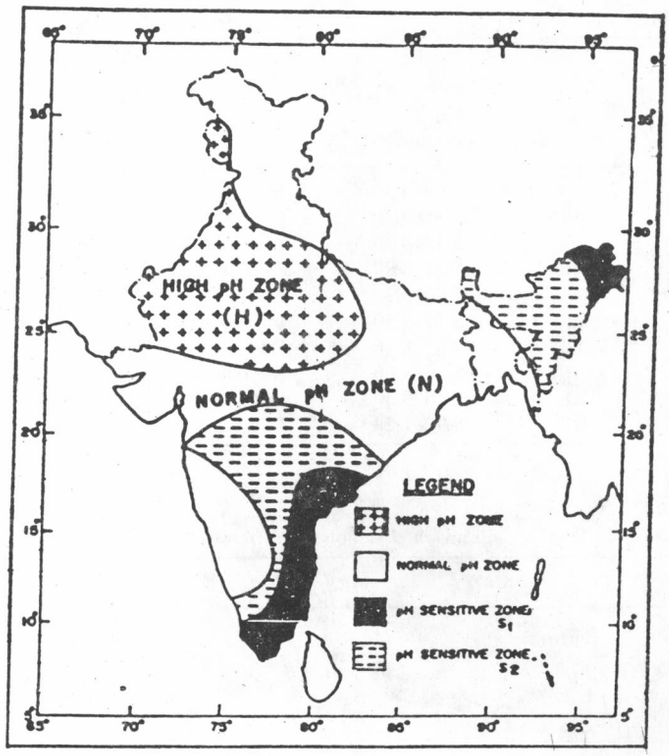

Figure 1. Rainfall-pH zoning in India[2].

Table 5. Annual 1978 mean pH values for BAPMoN stations in different countries

Country	Mean pH	Remarks
Canada	4.23–5.96	–
Czechoslovakia	4.18–4.34	–
Denmark	4.25	Data from one station only
El Salvador	5.40	Data from one station only
Facroe Island	4.46	Data from one station only
Finland	4.34–4.74	–
France	4.39–5.25	–
G.D.R.	4.05–4.25	–
Greenland	4.39	Data from one station only
Hungary	5.11	Data from one station only
Ireland	5.17	Data from one station only
Italy	5.10–6.37	–
Japan	4.83	Data from one station only
Malaysia	5.15	Data from one station only
Netherlands	4.46	Data from one station only
Norway	4.10–4.40	–
Poland	4.67	Data from one station only
Switzerland	5.83–6.09	–
Sweden	4.32–4.97	–
UK	5.23	Data from one station only
USA	4.15–6.19	–
USSR	5.78–6.64	–
Yugoslavia	4.73–4.88	–

in Chembur, Mumbai in 1989. A decreasing pH trend was observed in the rain water samples collected and analysed during 1963–1984 at Agra and 1965–1984 at Delhi. Average concentrations of major ionic components along with pH values are given in Table 6. Since

Table 6. The average concentration (μeq l^{-1}) at Agra and Delhi in the monsoon season in different years

	Agra		Delhi	
	1963	1984	1965	1984
Cations				
Na^+	94	101	80	76
K^+	51	41	11	33
Ca^{2+}	468	237	242	148
NH_4^+	11	18	13	29
SUM	624	397	346	286
Anions				
Cl^-	63	76	71	71
SO_4^{2-}	38	52	26	57
NO_3^-	11	40	–	–
SUM	112	168	97	128
pH	9.1	6.3	7.0	6.10
H^+	0.0008	0.5	0.1	0.79
OH^-	12.6	0.02	0.1	0.12

anions and cations do not balance, the phenomenon can be explained on the basis of missing anions HCO_3^- associated with Ca^{2+} and Mg^{2+} released from the soil dust. Subramanian and Saxena[17] have shown that HCO_3^- is a major anion at Delhi (270–103 meq l^{-1}) compared to Calcutta and Bhopal which is reported between 16–983 and 39–525 meq l^{-1} (ref. 18). pH values have declined by 0.9 and 2.8 in Delhi and Agra respectively. The decrease in pH at Agra is due to significant variation in the concentration of pollutants released from natural and anthropogenic sources. Due to the increase in industry at Agra in 1980s, the concentrations of acidic components (SO_4^{2-} and NO_3^-) have gone up by 88% whereas the concentrations of basic components Ca^{2+} have gone down by 50%.

Recent studies[19,20] show that pH values were observed below 5.6 in August and September at Delhi. Results of the experiment are shown in Table 7. In almost all events, the ionic balance was not achieved and the ratio between anions and cations was always below 1. Presence of HCO_3^- ion and organic ions may be the reason. In this analysis, it was found that as the precipitation amount increased, the cations and anions decreased but the hydrogen ion concentration increased. Similar results were reported at Western Arabian Gulf Coast. It is perhaps due to the washing off of atmospheric constituents in earlier rains. During monsoon, Delhi experiences winds from E/SE where major industries are located. The pollutants from these industries are transported and deposited over Delhi during this season. In other seasons, the cations from soil-derived dust are high enough to neutralize the acidity of the atmosphere. Though emissions are significant in India, presence of dust-derived cations is sufficient to neutralize acidic effect. However, localized effects are visible in areas near industrial belts. Deposition patterns are largely

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Table 7. Chemical composition of rain water observed at Delhi in 1991

	Cations				Anions		
	Min. (μeq l^{-1})	Max. (μeq l^{-1})	Avr. (μeq l^{-1})		Min (μeq l^{-1})	Max. (μeq l^{-1})	Avr. (μeq l^{-1})
H^+	0	43.65	63.0	Cl^-	0	493.65	119.59
NH_4^+	0	49.46	21.01	SO_4^{2-}	0	360.19	72.13
Na^+	0	290	73.4	NO_3^-	0	293.55	51.82
Ca^{2+}	0	477.04	118.86				
K^+	0	141.69	33.36				
Mg^{2+}	0	>1000	–				
pH	4.36	8.06	5.93				

determined by wind flow patterns as shown in Figure 2 (ref. 5).

In another significant study[16], the rainfall weighted pH values of 10 Indian BAPMoN stations from the period 1974–1984 have been used along with the pH values as determined by other researchers[21–26] in the different parts of the country and on that basis iso-pH curves have been drawn and finally the pH regionalization has been made. Accordingly, India can be divided into four such zones as follows (Figure 1):

(1) Highly sensitive pH zone (S1);
(2) Moderately sensitive pH zone (S2);
(3) Normal pH zone (S3);
(4) High pH zone (H).

In zones S1 and S2, the prime acid neutralizer, i.e. NH_4^+ and alkaline salts are less. The excess of anions over cations has been observed in the southern coastal belt region which are of marine origin[4] and therefore, more industries in this region would lead to greater probability of acid rain problem.

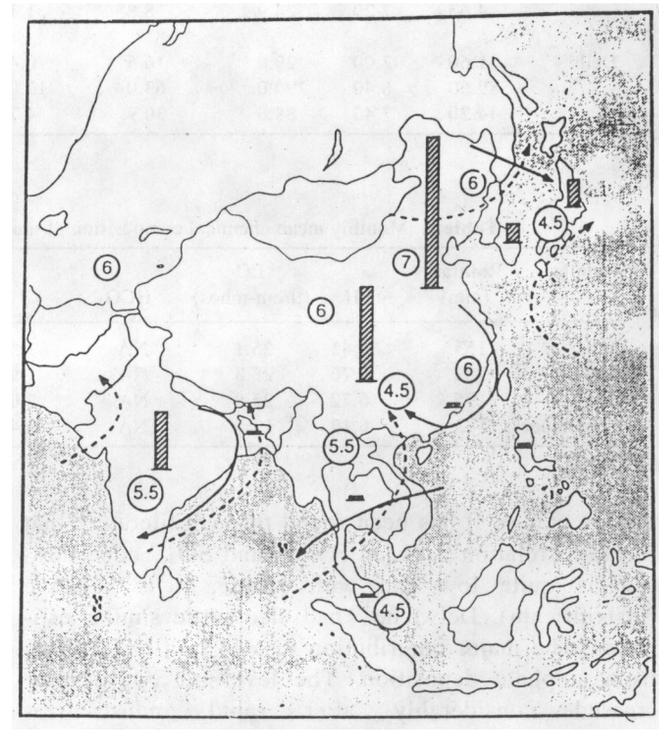

Figure 2. Acid deposition in Asia[5].

Chemical composition of rain water in India

Since rain water is a major atmospheric cleaning agent, the chemical composition of rain water will help in investigating the source regions, atmospheric transport, time of precursor as well as the deposition patterns. In India, the study of chemical composition of precipitation was started long ago[21,27–29]. During the last two decades, extensive work has been done[20,30–34] at various places in India. For the present study, five representative cities Bhopal (Madhya Pradesh), Calcutta (West Bengal), Delhi, Lucknow (Uttar Pradesh) and Pune (Maharashtra) are considered for the analysis[35]. Chemical composition of pre-major industrialization phase is summarized in Tables 8 and 9. Table 8 shows minimum, maximum and mean levels of annual rainfall, pH, conductivity, HCO_3^-, NO_3^-, SO_4^{2-}, Cl^-, Na^+, Mg^{2+}, K^+ and Ca^{2+} levels in rain water of a particular year.

It may be concluded that pH levels are in the 5.9–8.4 level with an average value of approximately 6.7. Levels of cations are quite high. HCO_3^- is a major constituent in all rain water samples. This ion is produced by the reaction of the carbonic acid with alkaline earth-bicarbonates present in the soil, dust or otherwise in the atmosphere as a particulate matter. Delhi has highest level of HCO_3^- due to proximity with Thar desert (Rajasthan). A study of ionic balance and its correlation with pH (individual samples) has been reported to indicate that with increase in excess of cations, pH values also increase. However, the linear correlation coefficient between these two parameters is not significant[36]. But simple correlation between excess of calcium with H^+ ion concentration and also between excess of sulphate (after subtracting the contribution from sea in Pune) and H^+ ion concentration is significant at 5 per cent and 1 per cent level respectively. It indicates that excess sulphate and calcium are able to influence the pH values to

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Table 8. Chemical composition (μeq l^{-1}) of rain water collected in five cities (Bhopal, Calcutta, Delhi, Lucknow and Pune)

	Rainfall (mm)	pH	EC (μ/cm-mhos)	HCO_3^-	Cl^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}
Bhopal	0.30	6.00	15.0	3.0	1.80	0.15	1.0	0.20	0.11	0.0	1.2
	223.40	7.10	80.0	32.0	8.20	2.20	12.0	4.30	2.11	1.2	5.0
	39.24	6.74	41.0	13.5	4.30	0.63	5.3	1.10	1.04	0.2	3.1
Calcutta	2.20	5.90	0.5	2.5	0.80	0.08	0.6	0.24	0.20	0.1	1.3
	289.9	7.30	60.0	19.0	9.80	0.90	12.8	1.95	4.20	0.9	4.8
	39.73	6.83	32.3	9.2	3.63	0.25	3.9	0.88	1.52	0.4	3.3
Lucknow	0.43	6.55	4.5	1.8	0.27	0.00	0.0	0.00	0.0	0.00	NA
	20.94	8.15	82.0	56.0	4.36	8.00	6.6	6.14	2.90	1.6	NA
	4.65	7.20	24.9	8.8	1.14	2.12	1.7	0.43	0.59	0.3	NA
Delhi	1.60	7.00	29.0	16.5	0.41	0.20	0.5	0.25	0.30	0.8	4.5
	89.60	8.40	290.0	63.0	17.0	2.50	13.0	5.50	10.4	9.9	88.5
	44.20	7.40	88.6	30.9	4.74	1.86	2.9	1.52	3.47	2.8	37.0

Table 9. Monthly mean chemical composition of monsoon rain water (μeq l^{-1}) collected at Pune, Maharastra

Months	Rainfall (mm)	pH	EC (μ/cm-mhos)	HCO_3^-	Cl^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}
June	153	6.41	25.1	NA	1.55	0.00	1.31	0.43	1.08	0.2	1.32
July	282	6.76	25.8	NA	1.95	0.84	1.34	0.48	1.47	0.2	1.05
August	95	6.72	25.8	NA	2.00	0.71	0.00	0.61	1.92	0.2	1.44
September	173	6.12	13.5	NA	0.45	0.58	0.49	0.16	0.37	0.3	1.20

a large extent. It has been found through literature that linear correlation between H^+ ion and SO_4^{2-} concentration is quite low and with nitrate, it is negative (insignificant). Delwiche[37] had also made similar estimates. The major contribution to acid rain is therefore from sulphate deposition. The level of SO_2 has increased considerably after rapid industrialization started. Table 5 shows that with increase in precipitation amount, cations and anions decreased but the hydrogen ion concentration increased. The dust particles play an important role in deciding the pH of rain water[34]. When the dust load increases, the pH increases, the main reason being the presence of more Ca^{++} and K^+ in dust. Thus the dust storms before the onset of monsoon result in high TSPM level in the ambient air which has neutralizing effect due to its alkaline nature. Therefore in July, the pH and both anion as well as cation concentrations were high but in subsequent rains (August and September), the hydrogen ion concentration increased while others decreased. It is due to scavenging in atmospheric constituents in earlier rains. The maximum rainfall occurs in these months in Delhi. During monsoon, Delhi experiences winds from east/south-east direction where major industries are located. Perhaps the pollutants from these industries are transported and scavenged over Delhi during the season. In other seasons, the cations from soil-derived dust are high enough to neutralize the acidity in the atmosphere.

Effect of acidity

A pH of 4.8 has been observed[3] at Chembur, Mumbai and 4.5 has been observed in Delhi[19,20]. Acidity at this level in soil, lakes and ground water can have adverse health effects directly as well as indirectly. The acidifying process taking place in the soil may increase the uptake of materials by plants, mostly in the form of positively-charged ions. Numerous hypotheses of the detrimental effects of acidic deposition on forest by soil-mediated mechanisms have been proposed. The main hypotheses are,

(1) Leaching of essential nutrients such as, K, Ca and Mg.
(2) Release of monomeric aluminium into the soil solution.
(3) Mobilization of trace metals.
(4) Reduction of the efficiency of mycorrhizae and
(5) Reduction of productivity of micro-organisms that decompose litter.

The effects of acidity in rainwater may adversely affect the eco-system. Thus these effects on selected flora and

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fauna could be used as bioindicators to assess the severity of the impact. Some of these are described below.

Effects on vegetation

(a) The plant's water uptake is most efficient with a soil pH value of 6 and above. For plant growth important nutrients are easily available and the most harmful metals are least absorbed at this pH.
(b) Damage may arise due to various factors explained and any one stress factor may sometimes trigger off a chain reaction between factors that created the necessary conditions for the symptoms to appear, that start damage and, those aggravating it.
(c) Direct effects harm needles or leaves when the protective layer of wax is corroded by the dry/wet acidic deposition.
(d) There may be damage to stomata which among other things regulate the evaporation of water. Membranes may also be injured inside the needle or leaf, causing loss of nutrient through leakage and upsetting the water balance.
(e) Indirect effect damages may occur when the ground gets acidic by the acid rain. The combination of an acidic environment with the toxic effects of the metals damage the roots[38]. As a result, the nutrient supply diminishes and toxic effect of aluminium makes the root hairs unable to take up sufficient water or nourishment.
(f) The mycorrhiza symbiosis of the root hair with fungi may be disrupted so as to impede, if not entirely cutoff the exchange of nutrients between the vegetation and the fungus.
(g) These effects impair the vitality of the vegetation also, and their ability to cope with disease and attacks by pests. Yellowing and browning of the needles at high altitudes, direct damage of leaves and needles[39] and growth of adventitious shoots, loss of root hairs and reduced root growth, shortened needles, narrower annual rings, a higher incidence of ruptures in trunk, and dropping of branches are some of the visible signs of vegetative decline[40].

Effects on aquatic ecosystems

(1) The first victims of acidification are crayfish, snails and mussels, certain types of macrophytes, zooplankton and phytoplankton and some species of mayfly[41].
(2) Salmon and trout, roach and minnow, and many sensitive insect species will be harmed if the pH drops to the 4.5–5 range[42]. All that usually remains are bog moss, the hardiest insects and certain species of plankton that are resistant to acidification.
(3) In acid lakes there are increasing concentrations of aluminium in ion form, which is highly toxic to many organisms[43]. The disappearance of fish is due to the combinations of a lowered pH and aluminium poisoning.
(4) The levels of other metals also rise, among them cadmium, zinc and lead are taken up to a greater extent by animals and plants. Not only the chemistry of water but, biological changes also take place due to destabilization of the eco-system.
(5) With the number of fishes reducing, certain insects on which they prey begin to thrive. Among those that specially benefit from the disappearance of the predators are certain water beetles and dragonfly larvae. In the absence of the fish, insects become more and more dominant than the fauna. These insects do not really thrive in acidic water but they multiply because their predators are gone.

Effects on human beings

(1) Acidic water liberates mercury from the soil. This can affect brain development during the foetal stage. Mercury is also absorbed by various plants, phytoplankton, small animals and these in turn are eaten by larger animals and with each higher step in the food chain, mercury gets bioaccumulated. When fish-eating birds and humans eat fish, they end up ingesting high levels of mercury[44].
(2) It is not likely that acid ground water by itself would be harmful to humans. But where the water is highly acidic, metals such as aluminium and cadmium may appear at elevated levels since they are released from the soil when the pH is less than 5. Cadmium is the most mobile of the ordinary heavy metals. It is one of the elements to which people have already been exposed to dangerously high concentrations. It accumulates in the renal cortex, causing lesions. It is moreover, an element that leaves the body very slowly. People who are already ingesting dangerous amounts of cadmium for instance, by smoking – will be at a grave risk if more cadmium gets through drinking water[45].
(3) Copper pipes are used for supply of drinking water at many places. Copper content in the water is responsible for diarrhoea in small children. Aluminium causes problems for kidney patients. In dialysis it enters the blood stream directly without first having passed the body's normal protective barriers. This may cause skeletal and brain injuries. It may also cause Alzheimer's and Parkinson's diseases which may lead to premature senility and death. Lead is also liberated by acidified water. It is liable to harm the nervous system, specially in children.

Critical load in India

Critical load is defined as the highest deposition level that is not likely to cause chemical changes leading to

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Table 10. Exceedance of area from critical level and cost of technology under three scenarios

Options and estimated cost	Percentage exceedance of area from critical level			
	1990	2000	2010	2020
Region: S–E Bihar and West Bengal				
Advance control technology available all over the world	50	55	85	90
Basic control technology	50	55	85	100
Locally available advance control technology	50	55	85	90
Region: Delhi				
Advance control technology available all over the world	0	0	15	85
Basic control technology	0	0	50	90
Locally available advance control technology	0	0	50	85
Cost of application (mio US$/yr)				
Advance control technology available all over the world	17.61	1834.22	3379.12	6337.29
Basic control technology	17.61	1887.35	3424.09	6213.49
Locally available advance control technology	17.61	1059.98	2023.77	3891.70

Table 11. Ambient SO_2 levels ($\mu g/m^3$) observed at various places in India during 1989*

State/Place	Latitude	Longitude	Minimum	Maximum	Average
Haldia (Bengal)	22°03'	88°05'	<1	105.6	12.4
Dhanbad (Bihar)	23°47'	86°26'	6.7	49.2	22.5
Calcutta	22°35'	88°14'	4.7	229.8	87.5
Delhi	28°39'	77°14'	3.0	46.7	9.9
Ahmdabad (Gujarat)	23°04'	72°38'	7.8	50.8	21.3
Faridabad (Haryana)	28°25'	77°28'	16.7	39.5	31.3
Bangalore (Karnataka)	12°58'	77°35'	8.8	101.9	33.4
Cochin (Kerala)	9°58'	77°16'	<1	51.8	10.6
Chennai	13°00'	80°11'	<1	133.9	22.5
Pune (Maharashtra)	18°32'	73°51'	<1	70.7	11.60
Bhilai (Madhya Pradesh)	21°13'	81°25'	<1	<1	<1
Talcher (Orissa)	20°58'	85°13'	1.8	57.2	30.0
Ludhiana (Punjab)	30°56'	75°52'	<1	<1	<1
Kota (Rajasthan)	25°11'	75°51'	3.6	65.5	20.4
Tuticorin (Tamil Nadu)	08°53'	78°8'	0.8	82.4	13.5
Agra (Uttar Pradesh)	27°10'	78°02'	3.3	42.7	19.7
Shimla (Himachal Pradesh)	31°06'	77°10'	0.6	28.4	3.5

*Data published by Central Pollution Control Board.

harmful effects on eco-system. By defining the relationship between the chemical status (base cation as well as aluminium concentration) and vegetation response, the critical load for that particular ecosystem can be derived. Critical load can be calculated by two methods,

(1) Relative sensitive approach: This method is based upon the climatic factors, factors relating to geology and soil characteristics, other geophysical features of an area, plant species and their tolerance ranges.
(2) Steady state mass balance model: It computes the critical load on the basis of the ability of a system to buffer the acidity due to supply of acidic compounds.

Both these approaches are used in the development of RAINS ASIA model[46] which is used for the present study. The sensitivity of terrestrial ecosystem in Asia to acidic deposition links different databases (soil, vegetation and climate) and focuses on vegetation as it is assumed that the fauna will be dependent on the changes in the vegetation structure and function, or be closely correlated to them. The buffering ability of the soil and vegetation tolerance range to changes in soil physico-chemical characteristics have been the basis for classification of sensitivity analysis and consequently, critical load determination. In the present analysis, focus has been on sulphur deposition as the sole acidic

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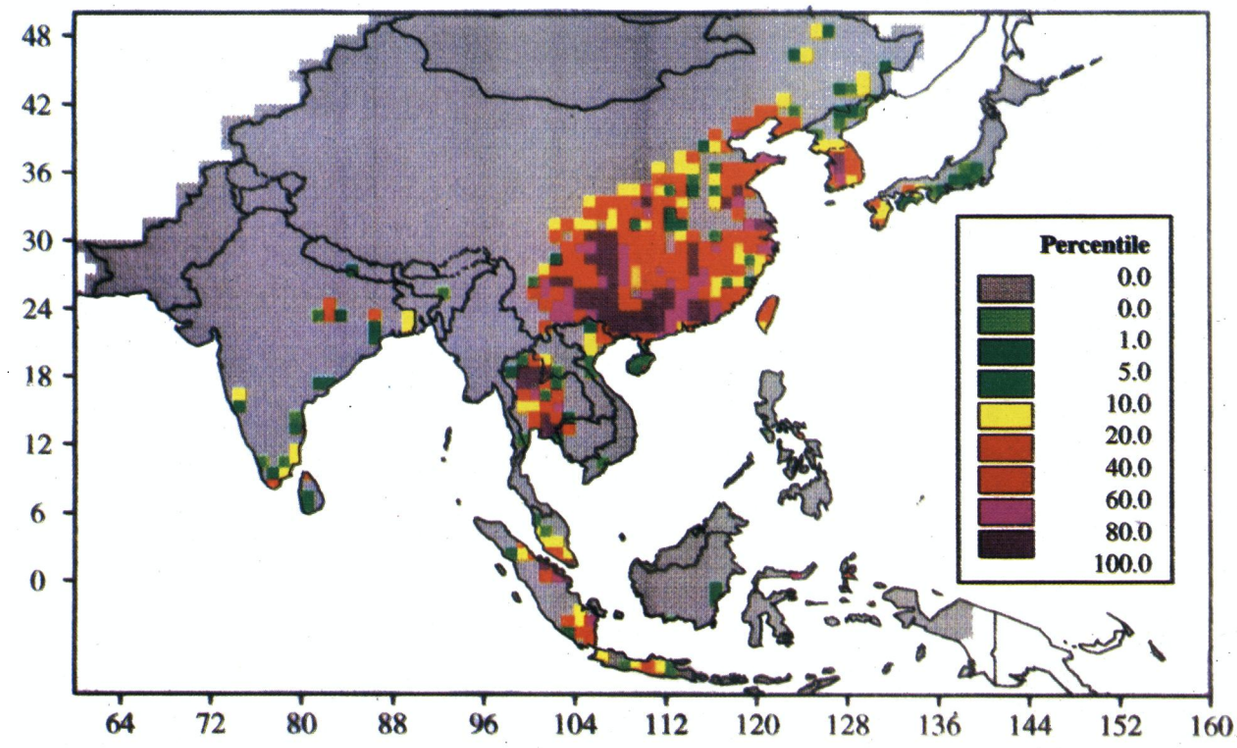

Figure 3. Exceedance of area 1995 (base: Basic Control Technology).

component. However, presence of NO_x can, in some cases, increase the acidic deposition. Mukhopadhyay *et al.*[34] found that the pH was highly related to nitrates in Indian BAPMoN stations. It is therefore envisaged that the overall impact will be much more than depicted in various figures and tables in this section. However, the same could be considered when the detailed source inventory for the entire Asian Continent as well as appropriate long range transport models are utilized. Further, the focus of attention has been on South Bihar, parts of West Bengal and Delhi. In the subsequent paragraphs, according to the inference derived from the model, results indicate that these areas are comparatively more vulnerable. Delhi is a rapidly-growing city which ranks fourth in the world in terms of pollution levels. It has an area of 1483 sq km with a total population of about 9.5 million and the highest population density of 6352 people per sq km in the country[47]. As Delhi is in the high pH zone (Figure 2), the overall impact here could be considered as localized in nature.

The critical load for Delhi for maximum allowable total acidic deposition with respect to the percentage of ecosystem threatened in various scenarios is given in Table 10. The ecosystems exceeding critical load due to sulphur deposition is projected to increase from 0% in 1990 to 15% in 2010 if Advanced Control Technology is used to control the emission. It may rise to 50% if only basic control technology is used for emission control. If the present trend continues unhindered, the ecosystem threatened may be well over 85% by the year 2020 even if the Advanced Control Technology is used to control the emissions. The estimated cost to use the Basic Control Technology, Advanced Control Technology available globally and Best Locally available technology to contain emission is given in Table 10. The long term damage to 50% of the ecosystem may prove detrimental since the effect of pollution and its level has already reached very high levels and a further damage means complete breakdown of the buffering ability and mitigating options.

A small area ($\simeq$ 400 sq km) in South Bihar as well as parts of West Bengal have been experiencing stress on their entire ecosystem with percentage exceedance of area from critical level reaching 50% by the year 2020. The expected SO_2 emission is likely to exceed 950 kt in Bihar, 550 kt in Bengal by the year 2010 and the corresponding figures projected for the year 2020 are 1550 kt and 1000 kt respectively (Table 1). The ambient air quality data published by the Central Pollution Control Board (CPCB) of India is given in Table 11. This shows that the limits prescribed by CPCB (30–80 $\mu g/m^3$-year) are already exceeding in Delhi and South Bihar–West

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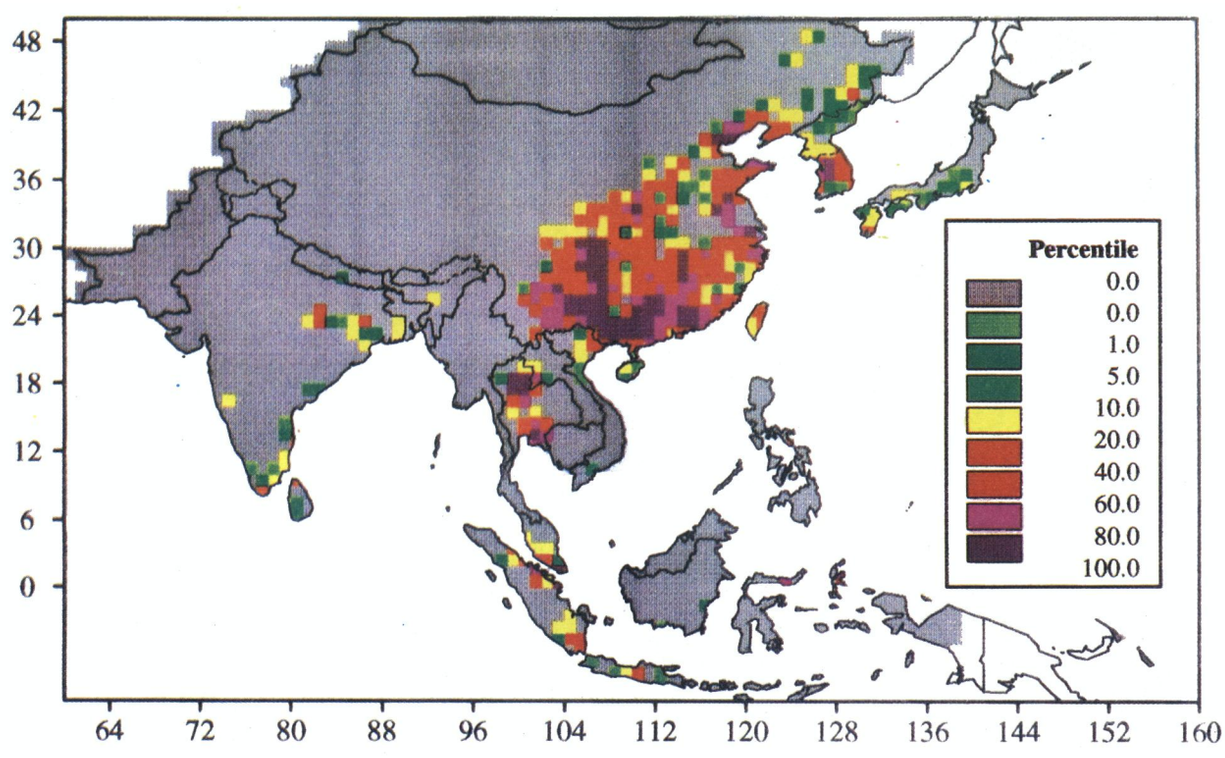

Figure 4. Exceedance of area 2000 (base: Basic Control Technology).

Bengal region. The main reason for South Bihar and parts of West Bengal facing such threats is due to the location of the largest coal belt and thermal power plants in the region. Further, there are several small-scale enterprises using coal as their energy input, not adhering to emission standards. Besides, frequent fire in coal mines may be one of the other reasons. However, the part of the north-east facing ecological stress is a critical problem. This area is very rich in forests and has diverse ecosystems of flora as well as fauna. Besides, this is also a tribal belt. Therefore, any destabilization will have ramifications on the socio-economic structure of the region and presumably, lead to vicious circle causing more destruction to the ecosystem.

In other parts of Asia, the highest emissions for SO_2 are found in south-east China, Bangladesh, Thailand, Korea, Indonesia and Japan (Table 2). The expected increase of emissions and the resulting excess of critical loads is already being used by China for location and relocation of emission sources, such that the distribution can have least impacts.

Future trends and policy requirements

Figures 3–5 show the acidic deposition in the year 1995 and its projection in 2000 and 2010 in the whole of Asia, when only basic control technology is used to control the emission pattern. Though the situation is well under control today in most parts of India except Bihar–West Bengal border, it is likely to worsen in many parts including Delhi, the north east, the southern parts and along the south east coast as well as parts of south west coasts in the near future. With commissioning of the Dhabol thermal power plant and Konkan Railway line, the south west region is likely to experience a sudden jump in its stress levels. Table 1 shows the sulphur emission expected in 1990, 2000, 2010 and 2020 if only basic control technologies are used to control the emission pattern of sulphur.

The existing regulations are not likely to change the scenario even if they are adhered to strictly. Though the best locally available control technologies can reduce the percentage ecosystem threatened considerably till the year 2010, the ecosystem might be considerably damaged after 2010 even on application of best available control technologies to reduce the emission. It is envisaged that by the year 2010, 50% of the area would be damaged when Locally Available Advanced Control Technology is used for Delhi and 85% in case of SE Bihar and West Bengal. Cost of application of adopting the various control technologies for the entire country is also included in Table 10. Therefore, it is desired that

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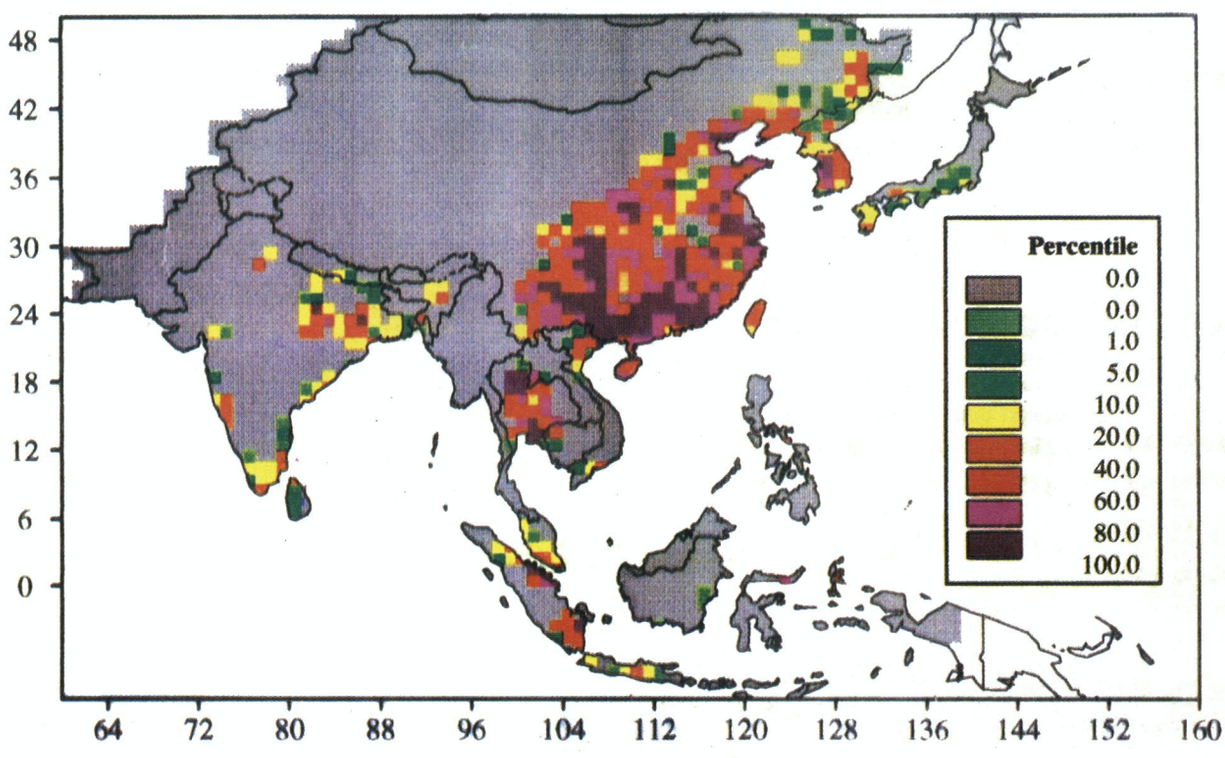

Figure 5. Exceedance of area 2010 (base: Basic Control Technology).

appropriate measures are taken to reverse the process. Among various other measures, proper siting of future industries and possibly part relocation of existing ones would be required to reduce the impact on the ecosystem by the year 2020. However, certain parts of South Bihar, parts of Bengal and north-east would still face strain on its ecosystems. It shows that the ecosystem has been considerably damaged already and the buffering ability is seriously hampered. Therefore, eco-rehabilitation of these areas would be helpful in reviving the ecosystem.

In light of the above facts, an early policy decision is required to stop acid rain in future. The phenomenon is localized and metropolises are more vulnerable to the effects of acid rain. Since the population density is quite high in metropolises, the sources of sulphur emissions are required to be well distributed instead of being localized. Power plants are to be sited away and expansion of industries responsible for sulphur emission in the vicinity of these metropolises should be stopped. India is a vast country and meteorological conditions differ a lot across the whole country. Since a single level for sulphur deposition cannot be defined for the whole country, sulphur levels for a host of places and the respective meteorological conditions are required to be defined. This is a complex process. But it is quite possible to mitigate acid rain phenomenon by such policy decisions.

The monitoring efforts so far are for research purposes and not as part of routine basis by regulatory bodies. Where localized effect is observed, monitoring should be done on regular basis. Since the effect is localized and low pH values are observed in many of the metropolitan cities where the population density is high, regular monitoring network is required. There cannot be a single value for pH of 5.6 to specify acid rain. For tropical countries, the equilibrium point of dissolution of CO_2 will be different and more research is required to specify the pH value representing acid rain. Also to be pointed out is the fact that the results obtained through theoretical models and projections were made on the basis of meteorological data of 1990 and the regulations which existed in 1990. Moreover, the effects due to other pollutants/precursors such as NO_x, NH_3, O_3, SO_4, etc. have not been considered. In addition, there may be shortcomings also such as inbuilt mechanisms to specify stress on an ecosystem through the critical load assessment methodologies which might have been outdated. Therefore, the effect of acid rain on flora and fauna should be monitored to assess whether any long-term effects due to acid rain exist or not. In summary, the following conclusions are drawn,

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1. The scenario is not grim considering that a large percentage of the country's area does not show unacceptable levels of sulphur deposition. The areas where serious impacts are expected seem to be manageable with proper measures.
2. The phenomenon is localized and the metropolises with high population density are more vulnerable to the effects of acid rain.
3. Power plants are to be sited away and expansion of industries responsible for sulphur emission in the vicinity of these metropolises should be stopped.
4. The sources of sulphur emissions are required to be well distributed instead of being concentrated and even relocated if necessary.
5. Efforts are needed for eco-rehabilitation in vulnerable areas like Orissa, South Bihar, West Bengal and metropolises. This can be achieved by improving basic facilities, stopping deforestation, taking up afforestation, change of fuel from cow dung, forest wood, etc. to bio gas, cooking gas, etc. and strengthening renewable sources of energy.
6. Since the sensitivity of terrestrial ecosystems to acidic depositions links different databases (soil, vegetation and climate) and focusses on vegetation, monitoring networks should be strengthened, more so in vulnerable areas to estimate the real effect on vegetation and human health through bioindicators.
7. The monitoring efforts related to wet and dry deposition of sulphur and other contributing species are so far made for research purposes only and not as part of routine basis by regulatory bodies. Hence, an elaborate monitoring network will give more accuracy in the prediction of acidic deposition and impact of other pollutants on acid rain.
8. The database in the country with respect to the land-use and forest cover needs to be updated, periodically examined and use of Geographical Information System could be made in this respect.

Finally, it is in order to mention a recent study of IIASA (International Institute for Applied Systems Analysis) for European Union (EU) for developing a strategy for combating acidification. This study shows that under a reference scenario based on current legislation and emission reduction plans, the critical loads for acidification will still be exceeded by 7% of the EU countries ecosystem area in 2010 compared with 24% in 1900 (ref. 48). Cost-benefit analysis of the various scenarios of this study revealed that in each case gains turned out to be greater than the cuts, despite the fact that many important items on benefit side were left out. The outstanding benefit in each case was the lessening of health effects as a result of reduced exposure to secondary air pollution[49]. Further, it is stated that since the benefits are largely ascribable to improvements in health, it can hardly be surprising that the greatest benefit should be recorded in countries with largest population.

Thus it could be concluded that it pays to reduce emissions and work out strategies to combat acidification.

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An advertisement inviting applications for a **Senior Scientist** position in the scale of Rs 16,400-450-20,000 in the National Institute of Oceanography (NIO), a constituent laboratory of the Council of Scientific and Industrial Research (CSIR) was published in *Curr. Sci.*, 1998, **74**.

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